

## SPECIFICATION

EXHAUST GAS PURIFICATION APPARATUS, EXHAUST GAS PURIFICATION  
METHOD, AND SULFUR COMPONENT TRAPPING AGENT FOR INTERNAL  
5 COMBUSTION ENGINE

## Technical Field:

The present invention relates to an exhaust gas purification  
apparatus and exhaust gas purification method for an internal  
10 combustion engine operated under a lean burn condition, wherein  
fuel is leaner than a theoretical air/fuel ratio.

## Background art:

In recent years, there have been attention to lean burn  
15 engines for lean fuel combustion in terms of an air fuel ratio.  
The air fuel ratio represents a ratio of air to fuel in gas.

Three way catalysts that have been used for exhaust gas  
purification of engines for theoretical air fuel ratio  
(stoichiometry) combustion have difficulty in purifying NOx.  
20 Thus, exhaust gas purifying catalysts for lean burn engines are  
investigated. One of them is disclosed in Japanese patent  
laid-open 11-319564(Patent publication 1) is disclosed. The  
publication discloses one of NOx absorbing metal oxides  
selected from alkali metals, alkaline earth metals and rare  
25 earth metals and a noble metal supported on a porous support.

According to the publication, NOx is effectively purified in a lean state of the air fuel ratio by using the catalysts. However, it has been known that since the exhaust gas from the lean burn engines contains SOx derived from sulfur contained in gasoline, activity of the catalysts is deteriorated by SOx,  
 5 which reacts with components in the NOx trapping catalysts.



(M: alkali metals or alkaline earth metals)

When the catalytic activity by sulfur component happens, it has been contemplated that the catalysts are exposed to gas of high  
 10 temperature and rich or stoichiometric s air fuel ratio so as to carry out a reaction shown by the formula (2), thereby to regenerate the catalyst by desorbing the sulfur component (S purge).



(M: alkali metals or alkaline earth metals)

In addition to the S purge, a method for controlling absorption amount of SOx is disclosed in Japanese patent laid-open 8-192051 (Patent document 2) wherein composite oxides  
 20 of Ti and Zr are used as a support whereby the activity of the NOx trapping catalysts is maintained even if sulfur components are present in the exhaust gas.

Further, Japanese patent laid-open 11-169708 (Patent document 3) discloses a SOx trapping agent is disposed before  
 25 the NOx trapping catalyst, thereby to trap SOx at the time of

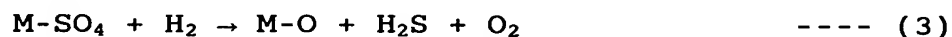
lean air fuel ratio and release SOx at the time of rich air fuel ratio, whereby an amount of inflow of sulfur components is reduced to suppress the sulfur poisoning to the NOx trapping catalysts or NOx purification catalyst.

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#### Description of invention:

The S purge makes fuel cost worse because it employs rich air fuel ratio. When a large amount of sulfur components adheres to the NOx trapping catalyst or NOx purification catalyst, an amount of a reducing agent for removing sulfur components as the amount of adhered sulfur components increases. As a result, a degree of rich air fuel ratio becomes large (the air fuel ratio becomes small), which makes the fuel cost worse. Further, once a large amount of sulfur components adhere to the NOx trapping catalyst, sulfur components that strongly react with the NOx trapping agent are hard to be removed thereby to lower the purification performance.

On the other hand, at the time of regeneration of NOx catalysts, sulfur components react with hydrogen, etc contained in the exhaust gas and exhausted as hydrogen sulfide (H<sub>2</sub>S) as shown in the formula 3, which makes the exhaust gas smell.



According to the technologies disclosed in Japanese patent laid-open 8-192051 (Patent document 2), adhesion of sulfur components to the NOx trapping catalyst at the time of lean air

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fuel ratio is suppressed and NOx trapping performance becomes lower.

According to the technologies disclosed in Japanese patent laid-open 11-169708 (Patent document 3), though an amount of  
5 inflow of sulfur components at the time of lean air fuel ratio, the sulfur components are released from the SOx trapping agent disposed in front of the NOx trapping catalyst at the time of rich air fuel ratio, and the NOx catalyst is sulfur poisoned by the released sulfur. Accordingly, S purge is necessary, which  
10 leads to the above problem, however.

Further, regeneration of sulfur trapping agent is necessary at the time of rich air fuel ratio where sulfur components are released, sulfur components are discharged though a NOx trapping rate of NOx trapping catalyst increases.

15 In addition to the above, since development for increasing a NOx purification rate under lean burn conditions has been made, an exhaust gas purification systems that does not discharge sulfur components has never been investigated. Since regeneration of NOx trapping catalyst and sulfur trapping agent  
20 release sulfur components, these sulfur components should be controlled.

An object of the present invention is to provide a sulfur component trapping agent that removes the above-mentioned disadvantages and can trap sulfur components for a long time,  
25 an exhaust gas purification apparatus and an exhaust gas

purification method.

The present invention relates to an exhaust gas purification apparatus for an internal combustion engine capable of lean burn operation at an air fuel ratio leaner than the theoretical air  
5 fuel ratio (18 or more), which comprises an exhaust gas passage of an internal combustion engine into which exhaust gas of an air fuel ratio of 14.7 or less flows, an NOx purification catalyst for trapping NOx in the exhaust gas at the time of lean air fuel ratio, and a sulfur component trapping agent, disposed  
10 in a previous stage of or before the NOx trapping catalyst, for capable of trapping sulfur components in the exhaust gas, wherein the sulfur trapping agent does not desorb (or does not substantially release) at the time of rich or stoichiometric air fuel ratio. The sulfur components include sulfur and sulfur  
15 compounds, which are derived from gasoline, light oil, lubricants, etc, and are present in the exhaust gas.

The words "does not desorb" are used to mean that a damaging amount of sulfur components are not released. For example, the sulfur component trapping agent exhibit a trapping rate of 85 %  
20 or more with respect to an inflow amount of sulfur components when gas composed of 150 ppm SO<sub>2</sub> - 5%O<sub>2</sub> - balance being N<sub>2</sub> is flown through the sulfur component trapping agent at an SV of 30,000/h and at 300 °C per 1.5 mol of the sulfur component trapping agent, and after the above test, the sulfur trapping  
25 agent exhibits an amount of 5 % or less of sulfur components

released from the sulfur component trapping agent per an amount of trapped sulfur components under conditions that a gas composition is 2000 ppmH<sub>2</sub> - 500ppmC<sub>3</sub>H<sub>6</sub> - 3000ppmO<sub>2</sub> - 3.5%CO - balance being N<sub>2</sub>, which is flown through the sulfur components trapping and temperatures are elevated from 300 to 750 °C at a rate of 10 °C/min.

Another feature of the present invention resides in providing an exhaust gas purification apparatus that installs a sulfur component trapping agent capable of sufficiently trapping sulfur components under rich or stoichiometric conditions.

A still another feature of the present invention resides in that a sulfur component trapping agent is disposed in the previous stage of the NO<sub>x</sub> trapping catalyst so as to suppress reduction of catalytic activity by the sulfur adhesion and a catalyst for oxidizing sulfur in the exhaust gas is disposed in the previous stage of the sulfur component trapping agent. The sulfur trapping agent includes a support that holds sulfur components in the exhaust gas.

As is disclosed in Japanese laid-open 11-169708, bonding power of SO<sub>2</sub> to the sulfur component trapping agent is weaker than that of SO<sub>3</sub>, and the sulfur components are hard to be trapped. This is because the number of oxygen atoms in SO<sub>3</sub> is large and because there is imbalance of electrons. Thus, acidity of the SO<sub>3</sub> is high. Accordingly, the sulfur components in the exhaust

gas are more easily trapped in the form of  $\text{SO}_3$  than  $\text{SO}_2$ , as shown in the formula 4.



Further, when  $\text{SO}_2$  gas enters the sulfur trapping agent, there is a possibility of reaction represented by the formula (5) in addition to the formula (2) thereby to produce sulfites as well as sulfates.



(M: metal atom for the sulfur trapping agent)

In general, sulfites are less stable than sulfates, and thus decomposition temperature of the sulfites is low. Accordingly, if sulfites are produced dominantly, a temperature of the exhaust gas elevates, and the temperature of the sulfur trapping agent elevates, decomposition reaction of the sulfites takes place thereby to release sulfur components from the sulfur trapping agent and to cause a problem that a  $\text{NO}_x$  trapping catalyst disposed at a post stage may be poisoned by sulfur components.

By disposing a catalyst for oxidizing sulfur components in the exhaust gas in front of the sulfur component trapping agent, sulfur components are trapped as  $\text{SO}_3$ . As examples of sulfur component oxidizing catalysts, noble metals such as Rh, Pt, Pd, etc, and any other catalysts that can oxidize sulfur can be employed.

Although a sulfur component trapping agent supported

together with sulfur component oxidizing component are supported on the same support may trap the sulfur components, such sulfur trapping agents are not proper if the sulfur oxidizing catalysts oxidize sulfur components and accelerate decomposition, which leads to release of sulfur from the sulfur component trapping agent.

The sulfur component trapping agent according to the present invention is featured by that the sulfur trapping agent is an oxide or carbonate of the metals and is capable of forming sulfates or sulfites that hardly release or discharge trapped sulfur components even when a temperature of the sulfur trapping agent elevates. The sulfur trapping agent is featured by sulfates of alkali metals such as Li, Na, K, Rb, Cs, etc, alkaline earth metals such as Mg, Ca, Sr, Ba, etc, or Ce, Al, Y, La, Ni, etc, which form sulfates having high melting points or high decomposition temperatures, and is also featured by not substantially containing such components as Ph, Pt, Pd, etc.

If the components such as noble metals that effect reaction of decomposition of sulfites are contained in the SO<sub>x</sub> trapping agent, the sulfur components trapped as the sulfites in the SO<sub>x</sub> trapping agent may be released in accordance with the formula (2) in a rich air fuel ratio. Accordingly, it is preferable that any components that contribute to decomposition reaction of sulfites are not contained in the sulfur component trapping agent. A preferable total amount of the noble metals should be

0.4 % by weight or less, and more preferably, 0.3 % by weight or less.

The present invention also relates to a filter, disposed in an exhaust gas passage of an internal combustion engine, for  
5 purification of exhaust gas from an internal combustion engine, a part of which carries a sulfur oxidizing catalyst and the other part of which carries a sulfur component trapping agent. The present invention relates to an exhaust gas purification apparatus using the exhaust gas purification filter. The  
10 exhaust gas purification apparatus is featured by disposing the filter in such a manner that the exhaust gas is introduced into the sulfur component oxidizing catalyst side and discharged from the sulfur component trapping agent side.

The sulfur component oxidizing catalyst may be supported  
15 on the surface of the upstream side of the filter, which is a plate or shaped flat filter, as same as in diesel particulate filters.

The sulfur component trapping agent or the exhaust gas purification apparatus according to the present invention can  
20 suppress degradation of the NOx purification catalyst for the internal combustion engine, which is operated under the lean burn condition of which the air fuel ratio is leaner than that of theoretical air fuel ratio.

Further, the present invention can provide an internal  
25 combustion engine for automobiles and an exhaust gas

purification apparatus that has good fuel consumption, suppressed degradation of a NOx purification catalyst caused by sulfur component and a small amount of sulfur component emission.

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Brief description of drawings:

Fig. 1 is an arrangement of a NOx trapping catalyst, sulfur component trapping agent and sulfur component oxidizing catalyst.

10 Fig. 2 is a graph showing a SOx trapping rate with respect to disposition and non-disposition of the sulfur oxidizing catalyst.

Fig. 3 is a graph showing release of H<sub>2</sub>S from sodium sulfate.

Fig. 4 is a graph showing release of SO<sub>2</sub> LiPt/Al<sub>2</sub>O<sub>3</sub>.

15 Fig. 5 is a graph showing a sulfur release rate with respect to a content of Rh + Pt + Pd.

Fig. 6 is a diagrammatic view of a DPF wherein the sulfur component oxidizing catalyst is supported on the upper-stream side of DPF and the sulfur component trapping agent is supported  
20 on the down-stream side of the DPF.

Fig. 7 shows an arrangement of the sulfur component trapping agent, which is disposed immediately after the engine.

Fig. 8 is a graph showing degradation of NOx trapping catalyst 1 depending on time.

25 Fig. 9 is a graph showing relationship between a sulfur

trapping rate by the sulfur component trapping agent and sulfur purge frequency.

Fig. 10 is a graph showing an amount of sulfur component on the NO<sub>x</sub> trapping catalyst depending on gas atmosphere.

5 Fig. 11 is a graph showing regeneration of the sulfur component trapping agent by sulfur purging.

Fig. 12 is a diagrammatic view of the exhaust gas purification apparatus according to the present invention.

10 Best embodiments for practicing the invention:

(Investigations of sulfur component trapping agents)

As the sulfur component trapping agents, components that hardly release and discharge sulfur components even when a temperature of exhaust gas changes, which leads to temperature  
15 change of the sulfur component trapping agent were investigated.

Since the temperature of the exhaust gas varies from room temperature to 650 °C, the sulfates of the sulfur component trapping agents should preferably have a melting temperature  
20 or decomposition temperature of 750 °C or higher. When the melting temperature or decomposition temperature of the sulfates is 750 °C, decomposition of sulfates hardly occurs and release and discharge of sulfur components are prevented. Table 1 shows melting points or decomposition temperatures of various  
25 sulfates (Refer to Chemistry Encyclopedia: Basic Version II,

Japan Chemical Society, Maruzen Publishing Co.).

Table 1: Melting points and decomposition temperatures

Element for a sulfur trapping agent	Sulfate	Melting point (*; decomposition temperature)
Li	$\text{Li}_2\text{SO}_4$	1256
Na	$\text{Na}_2\text{SO}_4$	884
K	$\text{K}_2\text{SO}_4$	1069
Rb	$\text{Rb}_2\text{SO}_4$	1060
Cs	$\text{Cs}_2\text{SO}_4$	1010
Mg	$\text{MgSO}_4$	1185
Ca	$\text{CaSO}_4$	1450
Sr	$\text{SrSO}_4$	1605
Ba	$\text{BaSO}_4$	1580
Mn	$\text{MnSO}_4$	700
Ce	$\text{Ce}_2(\text{SO}_4)_3$	920*
Al	$\text{Al}_2(\text{SO}_4)_3$	770
La	$\text{La}_2(\text{SO}_4)_3$	1150*
Fe	$\text{Fe}_2(\text{SO}_4)_3$	480*
Y	$\text{Y}_2(\text{SO}_4)_3$	1000*
Zn	$\text{ZnSO}_4$	600*
Co	$\text{CoSO}_4$	735
Zr	$\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	380*
Cu	$\text{CuSO}_4$	200
Ni	$\text{Ni}_2\text{SO}_4$	848

From Table 1, it is considered that sulfates of alkali metals such as Li, Na, K, Rb, Cs, etc, alkaline earth metals such as Mg, Ca, Sr, Ba, etc and Ce, Al, Y, La, Ni, etc have high melting point or decomposition temperatures and they are suitable as the sulfur component trapping agents.

When the sulfur component trapping agent is the alkali metals or alkaline earth metals, for example, sulfates of the alkali metals or alkaline earth metals are produced by reaction according to the formula (1) when SO<sub>x</sub> contained in the exhaust gas in the lean air fuel ratio contacts with the sulfur component trapping agents.

As is discussed above, when the noble metals are present in the sulfur component trapping agents, release of sulfur components tends to occur at the time of rich air fuel ratio. Accordingly, the noble metals such as Rh, Pt, Pd, etc should preferably be not contained in the sulfur component trapping agents. A total amount of Rh + Pt + Pd should be 0.4 % by weight or less per a weight of the sulfur component trapping agent. An amount of the sulfur component trapping agents depends on kinds of fuels used and required performance.

Estimation on the total sulfur components exhausted from a diesel car for a running at a speed of 16000 km was made. If a fuel consumption is 20 km/L, an amount of light oil is 8000L. On the other hand, if a specific gravity of the light oil is 0.85g/cc and a concentration of sulfur components in the light

oil is 10 ppm, a total sulfur exhausted is 2.1 moles. Accordingly, in order to trap all of the sulfur, 4.2 moles of  $\text{Na}_2\text{CO}_3$  is required thereby to convert  $\text{Na}_2\text{CO}_3$  to  $\text{Na}_2\text{SO}_4$ , when  $\text{Na}_2\text{CO}_3$  is used as the sulfur component trapping agent.

5        On the other hand, when  $\text{CaO}$  is used as the sulfur component trapping agent, 2.1 moles of  $\text{CaO}$  is required to convert  $\text{CaO}$  to  $\text{CaSO}_4$ . Accordingly, when the alkali metals are used, at least 4.2 moles are necessary, and when the alkaline earth metals are used, at least 2.1 moles the alkali metals are necessary.

10       Although only the sulfur trapping components can be used in the sulfur component trapping agent, the sulfur trapping components may be supported on a porous support. The porous support may function to enhance dispersion of the sulfur trapping components. When the porous support is used, an amount  
15       of the sulfur trapping component, which is 0.2 mole part or less in a metallic element conversion per 1.9 mole parts of the porous support, is insufficient for sulfur component trapping performance if a large amount of sulfur components is generated. If the amount of the sulfur trapping component is 0.8 mole part  
20       or larger, the sulfur component trapping agent tends to cohere on the porous support thereby to decrease the sulfur trapping capacity. Accordingly, an amount of the sulfur trapping components is preferably 0.2 to 0.8 mole part per 1.9 mole parts of the porous support.

25       In the specification, the words "mole part" are used to

represent concentration rates of respective components in conversion of moles; if a supported amount of component B is 0.5 mole part per 1 mole part of component A, a mole ratio of the amount of B component to that of A component is 0.5, 5 irrespective of an absolute amount of A component.

The porous support may be supported on a substrate; in this case, a preferable supporting amount of the support is 30 to 400 g per 1L of the substrate for the sulfur component trapping performance. If the supporting amount of the porous support is 10 less than 30 g, the performance of the porous support will be insufficient, and if the supporting amount of the porous support is larger than 400 g, the specific surface area of the porous support itself becomes small. The above are not preferable.

If the amount of the porous support is too small, a sulfur 15 trapping amount becomes small, and if the amount is too large, the specific surface area of the porous support becomes small.

As the porous supports, there are metal oxides or composite oxides of alumina, titania, silica, silica-alumina, zirconia, magnesia, etc. Alumina is particularly suitable because it is 20 good in heat resistance and has a function of good dispersion of the sulfur trapping components thereon.

Various shapes of the sulfur component trapping agents and sulfur oxidizing catalysts may be employed in accordance with applications. Honeycomb structures produced by coating the 25 sulfur component trapping agent and the sulfur component

oxidizing agent on a honeycomb substrate made of cordierite, SiC, stainless, etc, or pellets, plates, granules, powders may be used. In the case of honeycomb structures, cordierite is the most preferable. However, if there is a possibility of  
5 temperature elevation of the catalyst, metallic substrates, which hardly react with the catalysts, would bring about good results. Further, it is possible to produce honeycombs made of only the sulfur component trapping agents and the sulfur component oxidizing agents.

10 (Investigations on NO<sub>x</sub> purification catalyst components)

Any NO<sub>x</sub> trapping catalysts that trap and purify NO<sub>x</sub> can be used; NO<sub>x</sub> trapping catalysts comprise at least one selected from alkali metals and alkaline earth metals and a noble metal, which trap NO<sub>x</sub> at high efficiency and high NO<sub>x</sub> purification  
15 performance.

Methods for preparing the catalysts include physical preparation methods and chemical reaction preparing methods such as impregnation methods, mixing methods, co-precipitation methods, sol-gel methods, ion-exchange methods, evaporation  
20 methods, etc.

As starting materials for the exhaust gas purification catalysts, various compounds, metals and metal oxides such as nitrate compounds, chelate complex compounds, hydroxides, carbonates, organic compounds, etc can be used.

25 (Investigations on trapping amounts in rich air fuel ratio)

Most of sulfur components in the exhaust gas are present in a form of SO<sub>x</sub> when the exhaust gas is in a lean air fuel ratio. On the other hand, when the air fuel ratio is rich, it is conceived that the sulfur components are present mainly as H<sub>2</sub>S.

5 Since a period of the rich air fuel ratio is shorter than that of the lean air fuel ratio, a large reduction in trapped sulfur components is not required unless the trapped sulfur components are released in the lean air fuel ratio. The reduction rate is defined as an amount of sulfur present after the sulfur trapping agent / an amount of sulfur flowing into the sulfur trapping agent  $\times 100$  (%).

When sulfur components are present in the form of H<sub>2</sub>S, there is a case where degradation of NO<sub>x</sub> trapping catalysts by sulfur components is small. Considering that the NO<sub>x</sub> trapping

15 catalysts are degraded by the reaction represented by the formula (1), degradation of the NO<sub>x</sub> catalyst is less problematic even if the reduction in the trapped sulfur components is low, when the amount of the sulfur components that enter the NO<sub>x</sub> trapping catalysts at the time of rich air fuel ratio is small is lowered.

20 Accordingly, if there is almost no lean air fuel ratio condition in a running mode of the internal combustion engine, it is possible to reduce an amount of sulfur component trapping agents of the exhaust gas purification apparatus thereby to lower the cost of the apparatus and to save space thereof.

Such sulfur component trapping agents as to trap 60 % of the sulfur components entering the sulfur component tripping agents are preferably used. The trapping rate of 85 % or more is more preferable. That is, when a temperature of the sulfur component trapping agent is set to 300 °C and gas consisting of 150 ppm H<sub>2</sub>S - 0.5 % O<sub>2</sub> - balance being N<sub>2</sub> is flown at a space velocity SV of 30,000/h for 1 hour, a sulfur component trapping agent having a trapping rate of 60 % or more should preferably be used; 85 % is more preferable.

The present invention provides an internal combustion engine provided with the sulfur component trapping agent. The above-mentioned DPF is provided with a sulfur component trapping agent as an example for trapping sulfur components. Further, an internal combustion engine equipped with the above-mentioned sulfur component trapping agent and the catalyst in the exhaust duct is operated under a lean air fuel ratio, and then the operation is switched to a rich or stoichiometric air fuel ratio, followed by switching to lean air fuel ratio to perform purification of the gas. If poisoning of the NO<sub>x</sub> trapping catalyst proceeds, a temperature at the entrance of the NO<sub>x</sub> trapping catalyst is elevated and gas of a stoichiometric or rich air fuel ratio is flown thereby to release sulfur components from the NO<sub>x</sub> trapping catalyst and regenerate the catalyst.

(Embodiments)

In the following embodiments of the present invention will be described. The present invention is not limited to these embodiments.

5 (Preparation methods of NOx catalyst)

After a slurry containing alumina powder and a precursor of alumina adjusted with nitric acid was coated on a cordierite honeycomb (400 cells/ in<sup>2</sup>) and the coating was dried thereby to produce an alumina-coated honeycomb with an amount of alumina  
10 of 1.9 moles per 1 L of an appearance volume.

After the alumina-coated honeycomb was impregnated with a first impregnation component containing cerium nitrate, the honeycomb was dried at 120 °C, followed by calcining it at 600 °C for 1 hour. Then the Ce carrying honeycomb was impregnated with  
15 a second impregnation component mixture containing dinitrosodiamine platinum nitrate solution, dinitrosodiamine palladium nitric acid solution, rhodium nitrate solution and potassium acetate, and the honeycomb was dried at 200 °C, followed by calcining it at 600 °C for 1 hour. Then, the  
20 honeycomb impregnated with Ce, Rh, Pt, Pd and K was impregnated with a third impregnating component mixture containing potassium acetate, sodium nitrate, lithium nitrate and titanium sol. Thereafter, the honeycomb was dried at 200 °C, followed by calcining it at 600 °C for 1 hour. The potassium acetate in  
25 the second and third impregnation mixture was the same. At the

final step, the honeycomb was treated in an electric oven at 700 °C for 5 hours.

According to the above-mentioned procedure, a NOx trapping catalyst 1 was prepared wherein the composition was 190 g of alumina, 27 g of Ce, 12.4 g of Na, 15.6 g of K, 0.4 g of Li, 4.3 g of Ti, 0.139 g of Rh, 2.792 g of Pt and 1.35 g of Pd, in conversion of elements.

(Preparation of sulfur component trapping agent)

Sulfur component trapping agents were prepared from Li, Na, K, Cs, Mg, Ca, Sr, Ba, La and Fe, respectively. The alkali metals were used in the form of carbonates, alkaline earth metals were in the form of oxides, and  $\text{La}_2\text{O}_3$  and  $\text{FeO}$ . Amounts of Li, Na, K, Cs, Mg, Ca, Sr, Ba, La and Fe were 1.5 moles per 1 liter of the honeycomb. In accordance with the same manner as in the preparation of the NOx trapping catalyst 1, sulfur component trapping agents were prepared wherein the above components were impregnated in the cordierite honeycombs to produce sulfur component trapping agents A, B, C, D, E, F, G, H, I and J.

(Embodiment 1: Installation of sulfur component oxidizing catalyst)

As shown in Fig. 1, the sulfur component trapping agent B ( $\text{Na}_2\text{CO}_3$ ) was installed before the NOx trapping catalyst 1 in an engine exhaust gas duct. Further, a sulfur component

oxidizing catalyst was disposed before the sulfur component trapping agent to constitute a purification apparatus. As the sulfur component oxidizing catalyst,  $\text{Al}_2\text{O}_3$  with Pt prepared in the same manner as in the method for preparing the  $\text{NO}_x$  trapping catalyst was used. The sulfur component oxidizing catalyst comprises 190 g of alumina per 1 liter of the honeycomb, 2.792 g of Pt, in conversion of elements.

In Fig. 1, a comparative embodiment 1 had no sulfur component oxidizing catalyst.  $\text{SO}_x$  containing lean gas was supplied to the sulfur component trapping agents to evaluate sulfur trapping rates by the sulfur component trapping agents.

Temperatures of the sulfur component oxidizing catalysts and sulfur component trapping agents were 400 degrees and 300  $^{\circ}\text{C}$ , respectively. A flow rate of  $\text{SO}_x$  containing lean gas was 3liters/min and concentration of  $\text{SO}_2$  was 150 ppm. The flow time was 1 hour.

The composition of the lean gas supplied to the sulfur component trapping agents is shown in Table 2. The sulfur component trapping rates were calculated by the equation (6) below.

Sulfur component trapping rate (%) =

(Sulfur amount of sulfur components trapped by the sulfur component trapping agent, mole)/an inflow amount of sulfur to the Sulfur component trapping agent, mole)  $\times 100$  (%)

----- (6)

Table 2: Lean gas composition

Gas components	Gas concentration (%)	Gas amount (mmol/h)
O <sub>2</sub>	5	401.8
N <sub>2</sub>	balance	balance
SO <sub>3</sub>	150 ppm	1.215

Fig. 2 shows sulfur component trapping rates in cases where the sulfur component oxidizing catalyst was disposed and was not. It is apparent from Fig.2 that the disposition of the sulfur component oxidizing catalyst exhibits higher sulfur trapping rates with the sulfur component trapping agent.

As is disclosed in Japanese patent laid-open 11-169708, it has been known that Pt functions as a sulfur component oxidizing catalyst. Accordingly, when the sulfur component oxidizing catalyst is disposed, SO<sub>2</sub> oxidation reaction takes place as represented by the formula (4), and the sulfur components entering the sulfur component trapping agent are mainly SO<sub>3</sub>. Since the bonding force of SO<sub>2</sub> to the sulfur component trapping agent is weaker than that of SO<sub>3</sub>, SO<sub>2</sub> is hardly trapped. Thus, sulfur components in the form of SO<sub>3</sub> are more easily trapped than in the form of SO<sub>2</sub> gas. Accordingly, the disposition of the sulfur component oxidizing catalyst before the sulfur component trapping catalyst improves the sulfur component trapping rates, as is apparent from Fig. 2.

performance of the sulfur component trapping agent)

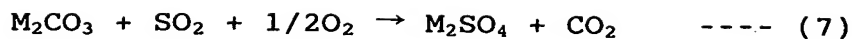
In the system shown in Fig. 1, amounts of sulfur trapped by the sulfur component trapping agent were calculated in a thermodynamic method when SO<sub>x</sub> containing lean gas was supplied to the sulfur component trapping agent. As calculation software, MALT2 (thermodynamic database for personal computer; Japan Society of thermodynamics) was used.

A temperature of the sulfur component trapping agent was 300 °C. A flow rate of the SO<sub>x</sub> containing lean gas was 3 L/min. The sulfur components in the gas were oxidized to SO<sub>3</sub> by the sulfur component oxidizing catalyst disposed before the sulfur component trapping agent. Thus, a concentration of SO<sub>3</sub> was estimated as 150 ppm. A period of flow time was 1000 hours. Gas components other than SO<sub>3</sub> were shown in Table 3. The sulfur trapping rates were calculated by the equation (6).

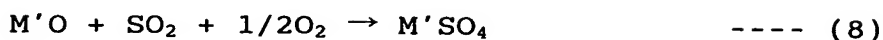
Table 3: Sulfur trapping rates of the sulfur component trapping agents A, B, C, D, E, F, G, H, I and J.

	Sulfur component trapping agent	Sulfur component trapping rate (%)
A	$\text{Li}_2\text{CO}_3$	100
B	$\text{Na}_2\text{CO}_3$	100
C	$\text{K}_2\text{CO}_3$	100
D	$\text{Cs}_2\text{CO}_3$	100
E	$\text{MgO}$	100
F	$\text{CaO}$	100
G	$\text{SrO}$	100
H	$\text{BaO}$	100
I	$\text{La}_2\text{O}_3$	100
J	$\text{FeO}$	0

From the above table, it is apparent that when the sulfur component trapping agents A to I are used, the sulfur trapping rates exceed 85%, which are sufficiently high. Accordingly, it is possible to sufficiently suppress the sulfur components entering the NO<sub>x</sub> trapping catalyst 1 disposed after the sulfur component trapping agent. Further, the sulfur component trapping agents A to I were converted into sulfates of alkali metals, alkaline earth metals and  $\text{La}_2\text{O}_3$  by virtue of trapping sulfur components. The sulfur trapping reactions of the alkali metals and alkaline earth metals with sulfur components may be represented by the following formulae.



(M: alkali metal)



(M': alkaline earth metal)

5     The melting points or decomposition temperatures of the  
sulfates of alkali metals, alkaline earth metals and La sulfate  
are higher than 750 °C; thus, once the sulfates are formed, they  
are not decomposed unless the temperature becomes above 750 °C.  
Accordingly, if the temperature of the sulfur component  
10   trapping agents is below 750 °C, the sulfur components trapped  
by they are not released again even when a normal temperature  
rise of the exhaust gas.

(Embodiment 3: Evaluation on decomposition sulfates of sulfur  
15   component trapping agents)

Decomposition of sulfates of the sulfur component trapping  
agents was evaluated. Sulfates/ $Al_2O_3$  prepared by drying and  
mixing various sulfates and  $Al_2O_3$  were used. A concentration  
of the sulfur component trapping agents per 10 grams of alumina  
20   was 0.04 mol in conversion of elements.

As samples of sulfates of the sulfur component trapping  
agents, sulfates of alkali metals, alkaline earth metals, and  
sulfates of Ce, Al, La, Y and Ni were chosen.

Powders of the above sulfur component trapping agents were  
25   granulated into 0.85 to 1.70 mm diameter. The temperature of

the sulfur trapping agents was kept at 300 °C and the rich gas shown in Table 4 was flown through the trapping agents, while elevating a temperature of from 250 to 750 °C. Concentrations of sulfur components (SO<sub>2</sub> + H<sub>2</sub>S) released from the trapping agents were measured. A space velocity SV of the gas was 30,000/h.

Table 4: Gas composition

	Composition (Rich air fuel ratio)
N <sub>2</sub>	Balance
H <sub>2</sub>	3000 ppm
CO	3.5 %
O <sub>2</sub>	3000 ppm
C <sub>3</sub> H <sub>6</sub>	600 ppm

Decomposition performance of the sulfur component trapping agents was calculated in accordance with the following equation.

$$\text{Sulfur component release rate (\%)} = \frac{(\text{an amount of sulfur released until 750 } ^\circ\text{C (mol)})}{(\text{an amount of sulfur trapped by the trapping agent mol})} \times 100 (\%)$$

----- (9)

The results are shown in Table 5 below.

Table 5: Evaluation on decomposition performance of sulfates of sulfur trapping agents

Sulfur trapping agent	Sulfate	Sulfur component release rate (%)
Li	$\text{Li}_2\text{SO}_4$	1
Na	$\text{Na}_2\text{SO}_4$	0
K	$\text{K}_2\text{SO}_4$	0
RB	$\text{Rb}_2\text{SO}_4$	0
Cs	$\text{Cs}_2\text{SO}_4$	0
Mg	$\text{MgSO}_4$	2.5
Ca	$\text{CaSO}_4$	2.5
Sr	$\text{SrSO}_4$	2
Ba	$\text{BaSO}_4$	1.5
Ce	$\text{Ce}_2(\text{SO}_4)_3$	4
Al	$\text{Al}_2(\text{SO}_4)_3$	4.5
La	$\text{La}_2(\text{SO}_4)_3$	3
Y	$\text{Y}_2(\text{SO}_4)_3$	3
Ni	$\text{NiSO}_4$	4.5

It is apparent from Table 5 that the sulfur component release rates of the sulfur component trapping agents are 5 % or less; the sulfur components trapped by the sulfur component trapping agents are hardly released and the trapping agents are suitable for the sulfur component trapping agents.

(Embodiment 4: Influence of coexistence of noble metals)

Influence of coexistence of noble metals and the sulfate ( $\text{Na}_2\text{SO}_4$ ) in the trapping agent B on decomposition of the sulfate was evaluated.

5         $\text{Na}_2\text{SO}_4$  was impregnated with a Pd solution, and the impregnated  $\text{Na}_2\text{SO}_4$  was dried at  $160^\circ\text{C}$ , followed by calcining it at  $600^\circ\text{C}$  for 1 hour. The resulting was mixed with dried  $\text{Al}_2\text{O}_3$  to prepare a Pd containing catalyst ( $\text{Na}_2\text{SO}_4\text{-Pd/Al}_2\text{O}_3$ ). A catalyst ( $\text{Na}_2\text{SO}_4/\text{Al}_2\text{O}_3$ ) was prepared in the same manner as in the above, 10 except for not containing Pd. The above catalysts were used in the evaluation. Concentration of Na and Pd were 0.04 mol of Na and 0.15 g of Pd per 10 g of  $\text{Al}_2\text{O}_3$ , in conversion of elements.

Powders of the above catalysts were granulated into 0.85 to 1.70 mm in diameter. The temperature of the catalysts was 15 kept at  $300^\circ\text{C}$  and rich gas was flown through the catalysts, while elevating temperatures from 250 to  $800^\circ\text{C}$  to measure amounts of sulfur components ( $\text{SO}_2 + \text{H}_2\text{S}$ ) released from the catalysts. The space velocity SV of the gas was 30,000/h.

Fig. 3 shows the results. In the case of Pd impregnation, 20 when the temperature of the catalysts exceeds  $500^\circ\text{C}$ , release of sulfur components was observed. This means decomposition of the sulfates. As the temperature of the catalysts elevates, amounts of released sulfur components increased; the amount of released sulfur components around  $750^\circ\text{C}$  was over 200 ppm.

25        On the other hand, in the case of the catalyst not containing

Pd, release of sulfur component was not observed when the temperature was elevated to 800 °C. In the case of Pd impregnation, an amount of released sulfur until 800 °C was 9 % per an amount of sulfur, which was originally contained in the catalyst. From the above fact, when Pd is impregnated, decomposition of sodium sulfate takes place at a temperature of 500 °C or higher.

If the noble metals and the sulfur component trapping agents are in contact, release of the trapped sulfur components occurs when the rich gas flows thereby to bring about poisoning of the NOx trapping catalyst 1. Accordingly, it is preferable that the sulfur component trapping agents do not contain noble metals.

(Embodiment 5: Influence of coexistence of noble metals)

Decomposition performance of lithium sulfate using a sulfur component trapping agent comprising LiPt/Al<sub>2</sub>O<sub>3</sub>, which was prepared in the same manner as of the NOx trapping catalyst, was evaluated. Additive amounts were 190 g of alumina per 1 L of the honeycomb, 1.8 g of Li and 2.792 g of Pt, in conversion of elements.

A temperature of the LiPt/Al<sub>2</sub>O<sub>3</sub> catalyst was set to 300 °C, and a lean model gas whose composition is shown in Table 6 was flown for 1 hour thereby to cause the catalyst to absorb sulfur components. Considering that the sulfur component trapping agent is installed in the system shown in Fig. 1, the sulfur

components to be flown through the trapping agent  $\text{LiPt}/\text{Al}_2\text{O}_3$  was  $\text{SO}_3$ .

While the rich gas whose composition is shown in Table 6 was being flown through the catalyst, the temperature of the gas was elevated from 300 to 700 °C; then concentrations of  $\text{SO}_2$  released from the  $\text{LiPt}/\text{Al}_2\text{O}_3$  catalyst were measured. The space velocity SV of the gas was 30,000/h at lean and rich conditions.

Fig. 4 shows the results. A peak is observed around 400 °C. It is assumed that the decomposition reaction of sulfates takes place around that temperature.

On the other hand, decomposition temperatures of  $\text{Li}_2\text{SO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$  are 1256 °C and 770 °C, respectively. Accordingly, it is conceivable that the decomposition of sulfate, which took place at 400 °C, was caused by Pt added to the catalyst. That is, when the noble metals and the sulfur component trapping agents are in contact, release of trapped sulfur components takes place at the time of flowing the rich gas thereby to bring about poisoning of the  $\text{NO}_x$  trapping catalyst. Accordingly, the sulfur component trapping agents should not contain the noble metals.

Table 6: Gas composition

	Gas composition	
	Lean	Rich
N <sub>2</sub>	balance	balance
CO <sub>2</sub>	10 %	12 %
H <sub>2</sub> O	10 %	10 %
H <sub>2</sub>	0 ppm	3000 ppm
CO	1000 ppm	6000 ppm
O <sub>2</sub>	5 %	5000 ppm
C <sub>3</sub> H <sub>8</sub>	500 ppm	600 ppm
SO <sub>3</sub>	150 ppm	0 ppm
NO	600 ppm	1000 ppm

(Embodiment 6: Quantitative influence of coexistence of noble metals)

- 5        A KNaRhPtPd/Al<sub>2</sub>O<sub>3</sub>, which was prepared in the same manner as in the method of preparing the NOx trapping catalyst 1, was used as the sulfur component trapping agent, and its sulfur component release performance was evaluated. Compositions of the trapping agents were 190 g of alumina per 1L of the honeycomb, 12.4 g
- 10    of Na and 15.6 g of K, in conversion of elements, and noble metals (Rh + Pt + Pd), wherein the total amounts of noble metals were 0 % by weight, 0.3 % by weight and 0.7 % by weight per the weight of the sulfur component trapping agent. Weight ratios of Rh, Pt and Pd were 1: 20: 10.

After the entrance temperature of the  $\text{KNaRhPtPd/Al}_2\text{O}_3$  was set to  $300\text{ }^\circ\text{C}$ , the model gas shown in Table 7 was fed though the sulfur component trapping agent for 2 hours, then the temperature was elevated to  $650\text{ }^\circ\text{C}$ , followed by letting the rich model gas flow for 10 min. Sulfur release rates were measured.

Considering that the sulfur component trapping agent is installed in the system shown in Fig. 1, the sulfur components entering the sulfur component trapping agent in lean air fuel ratio was  $\text{SO}_3$ . The space velocity SV of the gas in lean and rich periods was 30,000/h.

Table 7 (Gas composition)

	Gas composition	
	Lean	rich
$\text{N}_2$	Balance	balance
$\text{CO}_2$	10 %	12 %
$\text{H}_2\text{O}$	10%	10 %
$\text{H}_2$	0 ppm	3000 ppm
$\text{CO}$	1000 ppm	3.5 %
$\text{O}_2$	5 %	3000 ppm
$\text{C}_3\text{H}_6$	500 ppm	600 ppm
$\text{SO}_3$	300 ppm	0 ppm
$\text{NO}$	600 ppm	1000 ppm

The sulfur component release rates were calculated in accordance with the equation (10).

Sulfur component release rate (%) =

An amount of sulfur released from the sulfur trapping agent in a rich period (mol)/ an amount of sulfur released from the sulfur trapping agent in a lean period (mol)  $\times 100$  (%)

---- (10)

5        Fig. 5 shows the results. When the amount of Rh + Pt + Pd is 0.4 % by weight or less, the release rate of sulfur component is less than 2 %, and the sulfur component trapping agent exhibits a high sulfur component retention performance. Accordingly, in order to expect a high sulfur component  
10        retention performance, the total amount of Rh + Pt + Pd should be 4 % by weight or less.

(Embodiment 7: Support on a filter)

As a method of arranging the sulfur component oxidizing  
15        catalysts before and after the sulfur component trapping agent, a filter can be utilized. As the filter, there may be exemplified diesel particulate filters (DPF), which have been used for removing particle material (PM).

For example, the sulfur component oxidizing catalyst is  
20        supported on a surface of the upper stream side of the DPF and the sulfur component trapping agent is supported on a surface of the downstream side of the filter. By this arrangement, it is possible to oxidize the exhaust gas to form SO<sub>3</sub> when the exhaust gas enters DPF so that the SO<sub>3</sub> can be trapped by the  
25        sulfur component trapping agent. In this case, if the noble

metals are used as the sulfur component oxidizing catalyst, decomposition of sulfates of the sulfur component trapping agent does not take place and flowing-out of the trapped sulfur does not occur even when the air fuel ratio becomes rich, because  
5 the noble metals are not in contact with the sulfur component trapping agent.

When the sulfur component oxidizing catalyst and the sulfur component trapping agent are disposed with a distance, there may be a problem that the formed  $\text{SO}_3$  may adhere to a wall  
10 of the gas passage thereby to damage the gas passage; on the other hand, in the case of filters, the above problem may be removed, because the formed  $\text{SO}_3$  is immediately trapped. Since the both faces of the filters can be utilized, the space can be reduced, compared with the case where the sulfur component  
15 oxidizing catalyst and the sulfur component trapping agent are separately arranged.

The present invention can be applied to diesel exhaust gas, wherein PM contained in the gas includes solid substance such as soot, sulfates and mists, which contain sulfur components.  
20 When the filters are used, these solid and liquid sulfur components as well as sulfur components in the gas phase are removed thereby to remarkably increase trapping performance of the sulfur component trapping agent.

Any filters may be employed as long as they perform the above  
25 functions. Materials for the filters may include cordierite,

stainless steel, SiC, etc. Various shapes of the filters may be employed. For Example, cross sections thereof may be circular, rectangular, elliptic, etc.

The sulfur component oxidizing catalyst and sulfur component trapping agent may be supported on filters by any proper manners such as wholly or partially supported on the filter surface in accordance with objects expected.

Fig. 6 shows a sectional view of a DPF (diesel particulate filter), which employs the sulfur component oxidizing catalyst and the sulfur component trapping agent. The sulfur component oxidizing catalyst is supported on the upstream side face of the filter and the sulfur component trapping agent is supported on the downstream side face of the filter. When exhaust gas enters DPF, it is oxidized by the sulfur component oxidizing catalyst to form  $\text{SO}_3$  and the resulted  $\text{SO}_3$  is contacted with the sulfur component trapping agent. When the noble metals are used as the sulfur component oxidizing catalyst, the sulfates of the sulfur component trapping agent by the noble metals in the rich air fuel ratio condition does not occur and release of sulfur components does not occur as well, because the noble metals do not contact with the sulfur component trapping agent.

When the sulfur component oxidizing catalyst and sulfur component trapping agent are disposed separately, produced  $\text{SO}_3$  adheres to the passage walls thereby to degrade the passage material. However, in the above-mentioned filter PDF there is

no problem because the formed  $\text{SO}_3$  is immediately trapped.

Since the both faces of the filter are utilized, the space for the filter is smaller than the case where the catalyst and the trapping agent are separately disposed.

5     The exhaust gas from the diesel engines contains solid matters such as soot, sulfates, etc and mists. These substances contain the sulfur components. Since the filters can remove these solid or liquid matters as well as sulfur components in the gas phase, the sulfur component trapping performance is  
10    remarkably improved.

(Embodiment 8: Installment of the sulfur trapping agent just below an engine)

Fig. 7 shows a diagrammatic view of an arrangement where the  
15    honeycomb type sulfur component trapping agent is disposed just below the engine. The words "just below the engine" are used to mean a position which is as close to the engine as possible. For example, the position is within 1 m from an exhaust manifold entrance port. The  $\text{NO}_x$  trapping catalyst may be disposed  
20    vertically.

In disposing the sulfur component trapping agent beneath a floor, a space is necessary in the floor. On the other hand, in disposing the sulfur trapping agent below the engine the space in the floor is not necessary so that a car room becomes  
25    wide.

The exhaust gas from an engine contain, which condenses. If the sulfates are formed on the sulfur component trapping agent, the sulfates dissolve into condensed water, which may be discharged as sulfuric acid into the downstream. This  
5 phenomenon leads to corrosion of the passage and degradation of the NOx trapping catalyst disposed after the sulfur component trapping agent.

When the sulfur component trapping agent is disposed just below the engine, a temperature of the sulfur component trapping  
10 agent tends to elevate thereby to prevent condensation of water. When the sulfur component trapping agent disposed just below the engine is a honeycomb type structure, the condensed water does not stay in the honeycomb structure to prevent the above problem, because a direction of the gas passages is vertical  
15 the ground.

(Embodiment 9: Estimation of S purge frequency)

It is difficult to completely prevent sulfur components from entering the NOx trapping catalyst disposed after the sulfur  
20 component trapping agent. Accordingly, degradation of performance of the NOx trapping catalyst to which the sulfur components adhere after a lapse of a long period of time even when the sulfur component trapping agent is disposed; thus the NOx trapping catalyst should be subjected to S purge.

25 An SO<sub>2</sub> containing model lean gas whose composition is shown

in Table 6 was flown through the NOx trapping catalyst 1 so as to evaluate degradation of the catalyst by sulfur components. The temperature at the entrance of the catalyst was set to 300 °C, and the space velocity of the gas was 30,000/h. Fig. 8 shows degradation rates of catalytic activity of the catalyst with respect to treatment time. The NOx purification rate was calculated by the following equations.

$$\text{NOx purification rate (\%)} = \frac{\{(\text{an amount of NOx entered the catalyst within 1 min. after switching to lean condition}) - (\text{an amount of NOx flowing-out from the catalyst within 1 min. after switching to lean condition})\}}{\text{an amount of NOx flowing-out from the catalyst within 1 min. after switching to lean condition}} \times 100$$

---(11)

From the above results, it is apparent that when the SO<sub>2</sub> containing lean model gas is flown through the catalyst for 1 hour, the catalytic activity lowers to 40 %, which necessitates S purge.

When a lean model gas containing 300 ppm of SO<sub>2</sub> is flown through the catalyst for 1 hour, an amount of entering sulfur components is 2.4 mmoles. Estimation of an amount of sulfur components entering the catalyst in a conventional exhaust gas purification apparatus is made under conditions that a concentration of sulfur components in gasoline is 10 ppm and fuel consumption is 10 km/L, the above entering amount of sulfur

components is equivalent to a running for 90.6 km. Accordingly, one S purge is required for every 90.6 km running.

If the S concentration in the exhaust gas is lowered by the sulfur component trapping agent in the system shown in Fig. 1 to thereby lower the S concentration of the gas entering the catalyst 1 to 1.5 ppm, the S purge is required for every 9060 km. In accordance with the above theory, relationship between calculation results of trapping rates of sulfur components in lean condition and frequency of S purge is shown in Fig. 9. The sulfur component trapping rate was calculated by the equation (6). The S purge frequency represents a distance between two S purges.

From Fig. 9, it is apparent that when the S trapping rate exceeds 85 %, the S purge frequency exceeds 604 km. Accordingly, this value is 6 times or more of that where the sulfur component trapping agent is not disposed. Thus, the advantage of the sulfur component trapping agent is remarkable.

(Embodiment 10: Evaluation of poisoning depending on gas atmosphere)

Lean gas and rich gas whose compositions are shown in Table 8 were flown through the NOx trapping catalyst 1 for 1 hour. A temperature at the entrance of the catalyst was 300 °C and the space velocity was 30,000/h. In the lean gas the sulfur components present in the form of SO<sub>2</sub>, and in the rich gas the

sulfur components present in the form of  $\text{H}_2\text{S}$ .

Table 8: Released gas from NOx trapping catalyst

	Gas composition	
	lean	Rich
$\text{N}_2$	balance	balance
$\text{CO}_2$	10 %	12 %
$\text{H}_2\text{O}$	10 %	10 %
$\text{H}_2$	0 ppm	3000 ppm
$\text{CO}$	1000 ppm	3.5 %
$\text{O}_2$	5 %	3000 ppm
$\text{C}_3\text{H}_6$	500 ppm	600 ppm
$\text{NO}$	600 ppm	1000 ppm
$\text{SO}_2$	150 ppm	0 ppm
$\text{H}_2\text{S}$	0 ppm	150 ppm

Fig. 10 shows amounts of sulfur adhered to the NOx trapping catalyst 1. When the catalyst is poisoned by  $\text{SO}_2$  (lean gas), the amount of adhesion of S is about 4 times that in case of poisoning by  $\text{H}_2\text{S}$  (rich gas). Accordingly, poisoning by the lean gas goes faster than in the case of the rich gas.

Suppose the sulfur component trapping agent is used in the system shown in Fig. 1. If a sulfur component trapping rate is 90 %, 10 % of sulfur components outflows from the sulfur component trapping agent. In view of facts that 90 % of the

sulfur component trapping rate is sufficient and the S poisoning by lean gas is 4 times that by rich gas,  $(100 - 10 \times 4 = 60 \%)$  or more of the trapping rate of the S component trapping trapped by the sulfur component trapping agent in case of rich gas is preferable.

(Embodiment 11: Spurge)

Elevation of temperature of the exhaust gas is necessary at the time of S purge. If the elevation is too much and the temperature exceeds the melting point or decomposition temperature of the sulfates, release of sulfur from the sulfur component trapping agent takes place. Accordingly, S purge should be carried out at a temperature as low as possible. For example, the S purge should preferably be carried out at a temperature of 500 to 700 °C at the NOx trapping catalyst entrance.

In the arrangement shown in Fig. 1, used were the Pt added  $\text{Al}_2\text{O}_3$  catalyst in Embodiment 1 as the sulfur component oxidizing catalyst and the trapping agent B as the sulfur component trapping agent. Under the same conditions as in embodiment 8, the NOx trapping catalyst 1 was subjected to S purge in the rich gas flow after the activity of the NOx trapping catalyst was decreased to 40 %. The rich gas whose composition is shown in Table 6 was supplied for 10 min to the NOx trapping catalyst 1 of which activity was decreased to 40 % at a temperature of

300 °C at the NOx trapping catalyst entrance. A temperature of the NOx trapping catalyst during the rich gas flow was 650 °C.

Fig. 11 shows the results. The NOx purification rate was calculated by the equation (11). Activity of the NOx trapping catalyst 1 was regenerated by flowing rich gas for 10 min to the activity before supply of the sulfur components.

In view of the fact that in embodiment 3, decomposition of the trapping agent B did not occur until 800 °C in addition to the above fact, it is apparent that release of the sulfur components from the sulfur component trapping agent does not occur thereby to regenerate the NOx trapping catalyst, when the temperature of the sulfur component trapping agent is set to 750 °C and the temperature of the NOx trapping catalyst 1 is set to 650 °C at the time of S purge.

(Embodiment 12: Diagnosis of degradation of sulfur component trapping agent)

Since the sulfur component trapping agent of the present invention is not one that is used and regenerated as in the conventional sulfur trapping materials, it is necessary to replace the sulfur component trapping agent with new one or a part of the exhaust gas purification apparatus is replaced. The present invention provides a system for indicating information on timing of replacement of the sulfur component trapping agent, wherein the degree of degradation of the sulfur component

trapping agent is estimated by the following method.

When the sulfur component trapping agent degrades, degradation of the NOx trapping catalyst disposed after the sulfur component trapping agent proceeds. Therefore, there is a correlation  
5 between the degree of degradation of the sulfur component trapping agent and poisoning speed of the NOx trapping catalyst by sulfur.

When S purge is applied to the NOx trapping catalyst, the degree of regeneration of activity of the NOx trapping catalyst  
10 greatly poisoned by sulfur is large. Accordingly, the degradation of the NOx trapping catalyst by sulfur can be estimated by the degree of regeneration of activity caused by S purge, and from that result degree of degradation of the sulfur component trapping agent can be estimated.

15 That is, when NOx purification rates after regeneration and before regeneration of the catalyst are measured and when a difference or a ratio between them becomes over a certain value, there is provided an apparatus for diagnosing degradation that indicates replacement of the sulfur component trapping agent  
20 and a replacement supporting system.

In order to make the replacement easy, the sulfur component trapping agent and a part of the NOx purification catalyst may be made detachable. According to the embodiment, the exhaust gas purification apparatus of the present invention can be used  
25 for a long time keeping effective purification performance.

(Embodiment 13: Constitution of internal combustion engine)

Fig. 12 shows a schematic diagram of an embodiment of an internal combustion engine equipped with the exhaust gas purification apparatus of the invention.

5       The exhaust gas purification apparatus of the invention comprises an engine 99, which is capable of lean burn combustion, an air-intake system comprising an air flow sensor 2, a throttle valve 3, etc; an exhaust gas system comprising an oxygen concentration sensor or A/F sensor 7, a gas temperature sensor 8 for a NOx trapping catalyst entrance, a gas temperature sensor 9 for a sulfur component trapping agent entrance, a temperature sensor 10 for a sulfur component trapping agent, the sulfur component trapping agent 12, a NOx trapping catalyst 13, a sulfur component oxidizing catalyst 14, a temperature sensor 15 for the sulfur component oxidizing catalyst, a temperature sensor 16 for the sulfur component oxidizing catalyst entrance, etc, a control unit (ECU) 11, etc. ECU is constituted by I/O for an interface of input and output, LSI, a calculation device MPU, memory devices RAM and ROM that memory a large number of control programs, a timer counter, etc.

25       The above-mentioned exhaust gas purification apparatus works as follows. An intake air amount into the engine is measured by the air flow sensor 2 after filtering with an air cleaner 1'. It flows through the throttle valve 3 and an injector 5 where the air is injected with fuel; then the mixed gas is supplied

to the engine 99. Signals from the air flow sensor and other sensors are input into the engine control unit ECU.

Running conditions of the internal combustion engine and conditions of the NOx trapping catalyst, etc are evaluated by ECU to decide air fuel ratio and injection time, etc of the injector 5 are controlled to concentration of the fuel to a predetermined values. The mixed gas intaken into cylinders is ignited by ignition plugs 6, which are controlled by signals from ECU 11 to combust air/fuel mixture.

Combustion exhaust gas is introduced into an exhaust gas purification system. The exhaust gas purification system is provided with the exhaust gas purification catalyst 13 for lean burn combustion, wherein NOx, HC and CO in the exhaust gas are purified by three way function of the catalyst in stoichiometric combustion running. In lean combustion running, NOx is purified by its NOx trapping function and HC and CO are purified by burning them by the catalyst. When the exhaust gas contains SOx, the sulfur components are oxidized by the sulfur component oxidizing catalyst and then almost all of the oxidized sulfur components is removed, followed by introducing the gas into the catalyst 13. If the catalyst 13 is partially poisoned by Sox to lower the NOx trapping performance, the NOx trapping performance of the catalyst 13, which is normally monitored during the lean combustion is recovered by shifting the air fuel ratio of the gas to a rich side in response to judging signals

and control signals from ECU. At the same time, the temperature of the catalyst 13 may be elevated in response to the judging signals and control signals from ECU to cause the sulfur components to release from the catalyst 13 so that the catalyst 5 13 is regenerated.

According to the above-described operation, exhaust gases over the entire operation conditions including lean and stoichiometric (including rich) operations are effectively purified.